

Synthesis and Application of Polyoxyethylene-Grafted Cationic Polyamidoamine Dendrimers as Retention Aids

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ABSTRACT: Novel derivatives of fifth-generation polyamidoamine, comprising polyoxyethylene macromonomer and acryloyloxyethyl trimethylammonium chloride units, were synthesized. The polyoxyethylene-grafted cationic polyamidoamine dendrimers were characterized with Fourier transform infrared, ¹H-NMR, ¹³C-NMR, and elemental analysis. The synthesis recipes and properties of the dendrimers were studied.

The retention efficiency of the dendrimers was determined and discussed. Highly effective retention aids were obtained in retention experiments with broadleaf wood pulp fibers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3468–3473, 2007

Key words: dendrimers; functionalization of polymers; modification; surfaces; synthesis

INTRODUCTION

Dendrimers are well-defined three-dimensional macromolecules. In recent years, they have been receiving increased attention, mainly because of their symmetry and high degree of branching and the high density of their terminal functional groups, which can participate in different reactions. Bonding a functional group to a dendrimer structure gives compounds new properties and new application areas.^{1–3} In the past 2 decades, hyperbranched polymers have been investigated as new retention systems that are superior to traditional linear polymers. Shin et al.⁴ studied the use of hyperbranched polyacrylamide (PAM) flocculation systems to improve retention during papermaking, and they suggested that their flocculation systems had a better retention rate of pulp fines and shear resistance than traditional linear PAM flocculation systems. Allen and Polverari⁵ investigated poly(propylene imine) (PPI) dendrimers as new retention aids in the production of newsprint, mechanical printing grades, and boards. The dendrimers were found to be very effective retention aids for fines, dispersed extractives, and ash in papermaking. They claimed that a retention system of dendrimers could increase not only the retention rate of pulp fines and fillers but also the paper machine dehydration velocity and

could effectively remove resin and plastic ropy materials. Koper⁶ described another investigation based on the effect of fifth-generation (G5.0) PPI dendrimers on the retention efficiency for calcium carbonate and pulp fines. Polyamidoamine (PAMAM) dendrimers are a family of water-soluble polymers characterized by a unique treelike branching architecture and a compact spherical shape in solution. Recently, Zhou et al.⁷ reported that PAMAM dendrimers served as flocculants in a study of a dye-producing wastewater treatment. Although past works have indicated that dendrimers could be effective retention aids for papermaking, the fundamentals of these systems have not been well studied. In recent years, our group has focused on developing new technologies for the flocculation behavior of dendrimers. We have synthesized a series of peripherally modified PAMAM dendrimers, including cationic, anionic, and nonionic water-soluble dendrimers.^{8,9} In addition, numerous research groups have concentrated their efforts on applying cationic dendrimers to drug carriers,¹⁰ gene delivery,¹¹ catalysis,¹² and light harvesting.¹³ In this article, we report the synthesis of G5.0 PAMAM-modified, poly(ethylene glycol) (PEG)-grafted cationic dendrimers containing polyoxyethylene (PEO) and acryloyloxyethyl trimethylammonium chloride (DAC) units in their peripheries. PEG is widely employed as a major component in modified dendrimers because of its good biocompatibility and solubility in various solvents.^{14–16} We chose polyoxyethylene macromonomers (PEO-A) based on the PEG chain length to enhance the formation of flocculation bridging. The retention efficiency of the PEO-grafted cationic dendrimers was investigated with manual papermaking experiments.

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EXPERIMENTAL

Materials

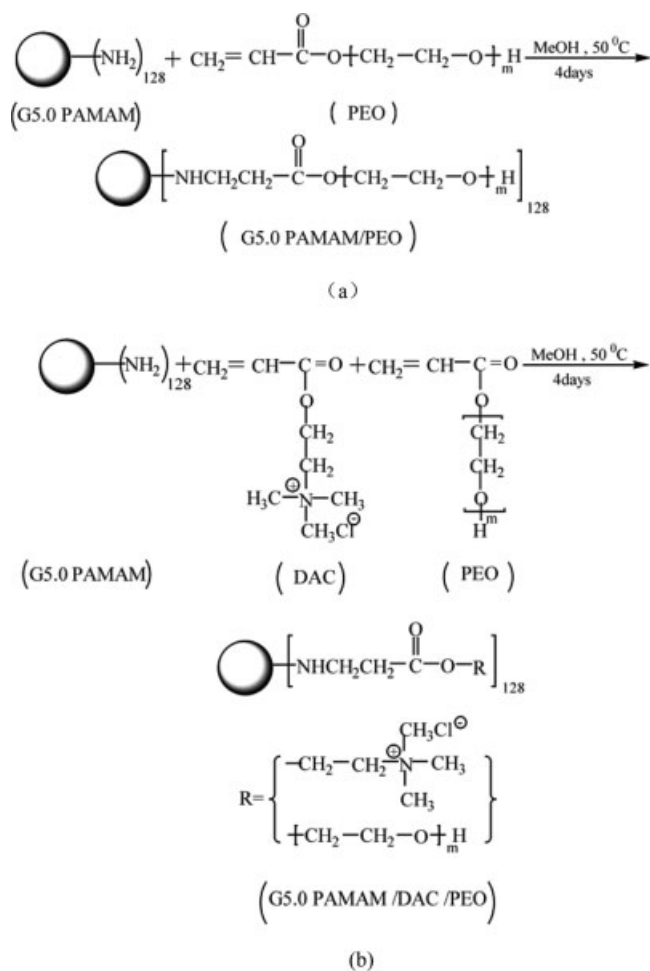
A G5.0 PAMAM dendrimer with an ethylenediamine core was prepared according to the method reported by Tomalia et al.¹⁷ DAC (France) and PAM (VN728; Guangzhou Fine Chemical Industry, Co.; viscosity-average molecular weight = 5.0×10^6) were commercial products and were used as received. PEO^a-A [*M_r* = 2054], PEO^b-A (*M_r* = 1554), PEO^c-A (*M_r* = 1054), PEO^d-A (*M_r* = 654), and PEO^e-A (*M_r* = 454) were prepared according to a reported procedure.⁹ Other organic reagents employed in this investigation were analytical reagents and were not further purified. The materials for the manual papermaking experiment were provided by the College of Resources Science and Papermaking Engineering, South China University of Technology (Guangzhou, China).

Synthesis of the PEO-grafted cationic PAMAM dendrimers

The synthesis of the G5.0 PAMAM/DAC/PEO dendrimers was carried out via a Michael addition reaction. The Michael addition reaction was conducted in a water bath at 50°C with a 500-mL, three-necked, round-bottom flask fitted with a condenser and magnetic stirrer under nitrogen. A G5.0 PAMAM dendrimer was dissolved in methanol to the appropriate concentration, and then the required amounts of DAC/PEO (or PEO) were introduced into the reaction vessel. After 4 days of reaction, the insoluble materials were filtered, and the residue was heated under reflux in 50 mL of diethyl ether for 30 min; the same process was repeated three times. The residue was filtered through an extended microporous polytetrafluoroethylene membrane. The purified product was dried in a vacuum oven at 40°C for 48 h and was obtained as a pale yellow or white, solid material. Scheme 1 presents the synthesis route of the G5.0 PAMAM/PEO and G5.0 PAMAM/DAC/PEO dendrimers.

Characterization of the PEO-grafted cationic PAMAM dendrimers

¹H-NMR and ¹³C-NMR spectra were recorded with a Bruker DRX-400 NMR spectrometer (Bruker, Ettlingen, Germany) with D₂O and CDCl₃ as the solvents, respectively. Fourier transform infrared (FTIR) measurements were carried out with a Nicolet Magna IR 760 spectrophotometer (Madison, WI) via the KBr pellet method. An elemental analysis was run on a PerkinElmer model 2400 instrument (Norwalk, CT). The particle size distribution of the dendrimers was determined with a Malvern (Malvern, UK) Autosizer Lo-C particle diameter distribution measuring appliance



Scheme 1 Surface modification of G5.0 PAMAM dendrimer with PEO (a) DAC, and (b) PEO.

with a laser of 670 nm at 25°C. The retention rate of the PEO-grafted cationic PAMAM dendrimers (the reference material was PEO-grafted PAMAM) was measured according to a literature method¹⁸ with a model 255 paper-forming instrument (Messmer Instruments) and a model PNP standard paper squeezer (Messmer Instruments).

RESULTS AND DISCUSSION

The synthesis of the PEO-grafted cationic PAMAM dendrimers was carried out through the grafting of monofunctional linear PEO arms and attached DAC groups to PAMAM dendrimer terminal —NH_2 groups via a Michael addition reaction. The synthesis routes of both G5.0 PAMAM/PEO^a (D-PEO^a-0) and G5.0 PAMAM/DAC/PEO^x (D-PEO^x-y; $x = a, b, c, d$, or e and $y = 1, 2, 3, 4, 5, 6, 7, 8$, or 9) are shown in Scheme 1.

The obtained dendrimers were characterized with FTIR, ¹H-NMR, ¹³C-NMR, and elemental analysis. The results for D-PEO^a-0 and D-PEO^a-1 are shown in Figures 1–3.

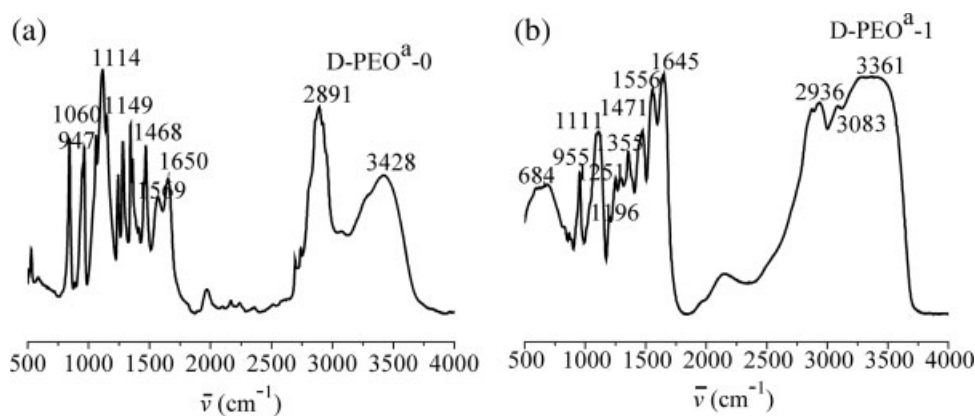


Figure 1 FTIR spectra of (a) D-PEO^a-0, and (b) D-PEO^a-1.

Figure 1 shows the FTIR spectra of D-PEO^a-0 [Fig. 1(a)] and D-PEO^a-1 [Fig. 1(b)]. In Figure 1(a), two peaks, one at 1650 cm⁻¹ (amide I) and the other at 1569 cm⁻¹ (amide II), are assigned to the asymmetric stretching vibration (C=O) and bending vibration (N-H) of HN-C=O. The peaks at 1149 and 1060 cm⁻¹ represent the stretching vibration of the -C-N- groups. The peaks at 2891 and 1468 cm⁻¹ are related to the stretching vibration of the -CH₂-

unit. The characteristic peaks of the ether group (-CH₂-O-CH₂-) can be found at 1114 and 947 cm⁻¹. They come from PEO-A, and the peak at 3428 cm⁻¹ is due to the stretching vibration of -OH groups, suggesting that a PEO chain is successfully attached to the amine-terminated group of the G5.0 PAMAM dendrimer. In a similar fashion, the amide I

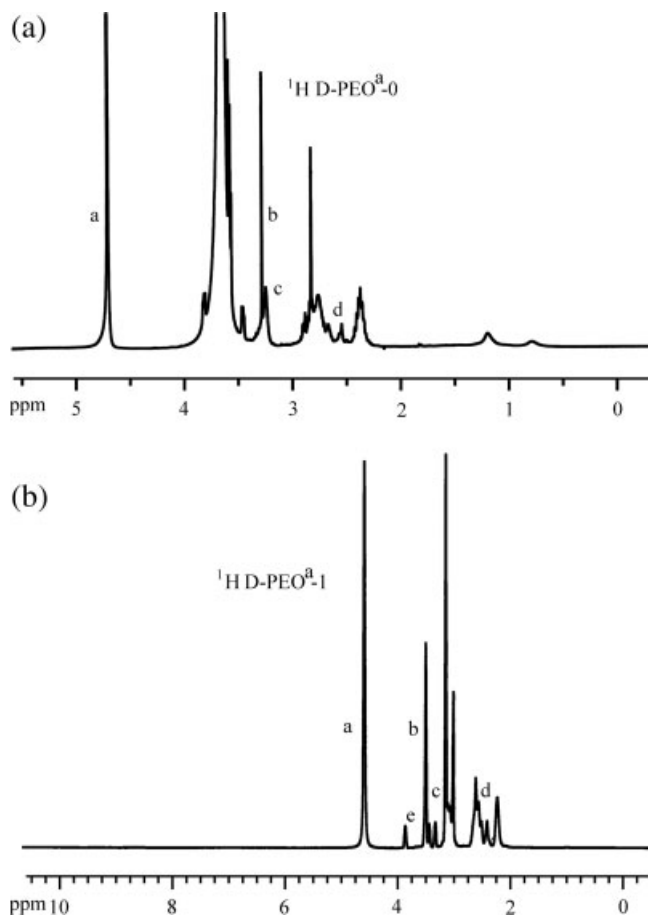


Figure 2 ¹H-NMR spectra of (a) D-PEO^a-0, and (b) D-PEO^a-1.

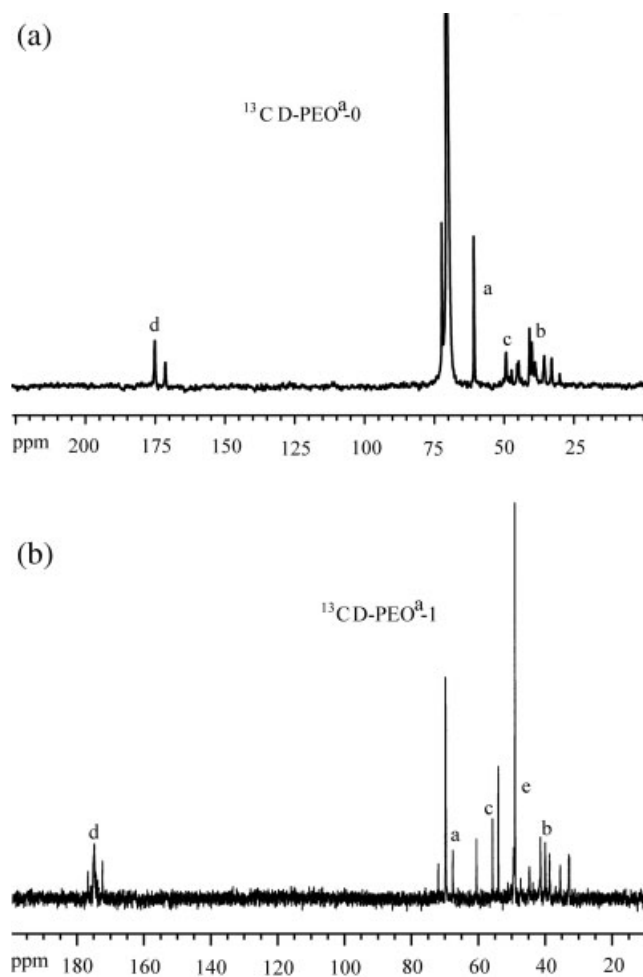


Figure 3 ¹³C-NMR spectra of (a) D-PEO^a-0, and (b) D-PEO^a-1.

TABLE I
Synthesis Recipes and Parameters of the Dendrimers

Sample	Monomer molar feed ratio (G5.0 PAMAM/DAC/PEO-A)	Conversion (wt %)	Mean dendrimer size (nm)	Polydispersity index
D-PEO ^a -0	1 : 0 : 256	82.5	41.3	1.001
D-PEO ^a -1	1 : 128 : 128	78.6	56.8	0.973
D-PEO ^a -2	1 : 44 : 212	65.2	60.6	0.998
D-PEO ^a -3	1 : 86 : 170	72.3	55.1	0.932
D-PEO ^a -4	1 : 170 : 86	78.2	53.2	0.976
D-PEO ^a -5	1 : 212 : 44	79.4	51.5	0.992
D-PEO ^b -6	1 : 128 : 128	77.9	49.6	0.960
D-PEO ^c -7	1 : 128 : 128	75.1	47.8	0.954
D-PEO ^d -8	1 : 128 : 128	76.3	46.9	0.972
D-PEO ^e -9	1 : 128 : 128	77.8	45.6	0.993

^a M_r for PEO = 2054.

^b M_r for PEO = 1554.

^c M_r for PEO = 1054.

^d M_r for PEO = 654.

^e M_r for PEO = 454.

and II bands are shifted to 1645 and 1556 cm^{-1} in Figure 1(b), respectively. These peaks change more strongly than those of D-PEO^a-0. The peaks of $-\text{CH}_2-$ groups are shifted to 2936 and 1471 cm^{-1} . The ether group peaks are shifted to 1111 and 955 cm^{-1} , and the peak of the $-\text{OH}$ groups is shifted to 3361 cm^{-1} . The characteristic peaks are all due to the PEO chain unit. In addition, a characteristic peak of quaternary ammonium groups at 3083 cm^{-1} [$\text{N}^+(\text{CH}_3)_3$] shows that the DAC chain is attached to the PAMAM dendrimer. These results show that the modified PEO-grafted cationic dendrimers were successfully synthesized.

¹H-NMR and ¹³C-NMR also provide evidence (see Figs. 2 and 3). In Figure 2(a), the ¹H-NMR spectra of the modified dendrimers of the single peaks at $\delta = 4.69$ ppm (a) are associated with PEO protons ($-\text{OH}$), and the peaks at δ values of 3.42 (b), 3.26 (c), and 2.56 ppm (d) are related to the methylene protons ($\text{CH}_2\text{CH}_2-\text{O}-$, $-\text{NHCH}_2-$, and $>\text{NCH}_2\text{CH}_2\text{N}<$, respectively). Similarly, corresponding peaks of the protons are at δ values of 4.70 (a), 3.55 (b), 3.22 (c), and 2.73 ppm (d) in Figure 2(b). Furthermore, the resonance of the methyl group protons ($-\text{CH}_3\text{Cl}^-$) that come from the DAC monomer is evidenced at $\delta = 3.82$ ppm (e). The results of the ¹³C-NMR spectral data (Fig. 3) are also depicted. The signals at δ values of 69.74 (a; $-\text{CH}_2\text{CH}_2-\text{O}-$), 42.23 (b; $-\text{NHCH}_2-$), 51.29 (c; $>\text{NCH}_2\text{CH}_2\text{N}<$), and 175.51 ppm (d; $-\text{CONH}-$) confirm the formation of these dendrimers in Figure 3(a), as well as those at δ values of 69.97 (a), 41.43 (b), 54.0 (c), and 174.17 ppm (d) in Figure 3(b). The characteristic peak of D-PEO^a-1 appears at $\delta = 49.4$ ppm (e) and represents the $-\text{N}-\text{CH}_3$ groups from the DAC monomer.

Elemental analyses proved that the compositions of both D-PEO^a-0 and D-PEO^a-1 corresponded to the calculated values:

- ANAL. Calcd for D-PEO^a-0 ($\text{C}_{13166}\text{H}_{26080}\text{O}_{6268}\text{N}_{506}$): C, 54.20%; H, 9.01%; N, 2.42%. Found: C, 54.18%; H, 9.03%; N, 2.46%.
- ANAL. Calcd for D-PEO^a-1 ($\text{C}_{7726}\text{H}_{15328}\text{O}_{3388}\text{N}_{570}\text{Cl}_{64}$): C, 53.73%; H, 8.94%; N, 4.62%. Found: C, 53.35%; H, 8.51%; N, 4.49%.

A similar procedure was carried out to characterize the other dendrimers. Table I shows the synthesis recipes and parameters of the dendrimers. The effects of the dendrimer composition on the product conversion and the properties were analyzed as follows.

The effect of the DAC content in the initial monomer molar feed on the dendrimer size and distribution can be seen in Table I (D-PEO^a-0, D-PEO^a-1, D-PEO^a-2, D-PEO^a-3, D-PEO^a-4, and D-PEO^a-5). The mean size decreased with increasing DAC content in the initial monomer molar feed. This was due to the fact that there were more DAC units than PEO-A chains in their peripheries. The sizes, which became larger than those reported,² were related to the aggregation interactions among the dendrimers. In Table I, we can also see that the dendrimer size increased with the increasing molecular weight of PEO-A in the initial monomer feed (D-PEO^b-6, D-PEO^c-7, D-PEO^d-8, and D-PEO^e-9), and this corresponded to the general macromolecular grafting law because the longer PEO-A molecular chain enhanced the thickness of the grafted surface layer. A narrow polydispersity index was also observed (Table I). Each value was approximately 1.0 (0.9–1.0) because they might have been

organized as very symmetrical, monodispersed arrays, as was the case for the dendrimers.

In addition to the aforementioned basic properties of the synthesized dendrimers, G5.0 PAMAM/PEO and G5.0 PAMAM/DAC/PEO were water-soluble dendrimers. They were insoluble in diethyl ether and petroleum ether but were highly soluble in carbon tetrachloride, trichloromethane, and water.

Retention efficiency of the PEO-grafted cationic PAMAM dendrimers

The retention experiments of the PEO-grafted cationic PAMAM dendrimers were performed according to a convention manual papermaking procedure. The effects of the retention rate for various mass fractions of retention aids are shown in Figure 4. During the initial stage, the retention rate sharply increased with an increasing mass fraction of the retention aid until the maximum value was obtained; this was followed by a decrease in the retention rate with an increasing amount of the retention aid. In this case, the effects showed a similar trend, but there seemed to be an optimum mass fraction of the retention aid. The optimum retention rate of D-PEO^a-1 [12.16 g (80 g/m²) of broadleaf wood pulp; 0.1% retention aid solution dosage; retention rate = $m_1/m_2 \times 100\%$, where m_1 is the dry mass of the paper and m_2 is the absolute dry mass of the broadleaf wood pulp] was 89.45% in a 0.2% mass fraction, but the rate was about 86.31% for D-PEO^a-0 in a 0.4% mass fraction and 88.24% for PAM in a 0.2% mass fraction. All these effects could be explained by the assumption that D-PEO^a-1 possessed a unique architecture that had not only the highly branched core-shell structure of dendrimers but also many long linear arms as well as the absorptivity of the cationic charge. The flocculation mechanism induced by D-PEO^a-1 was bridging formation

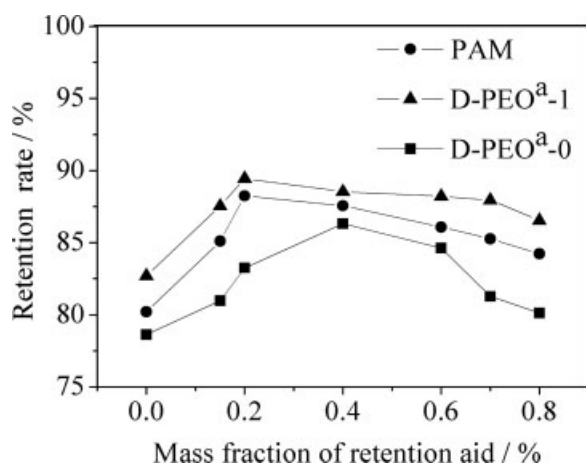


Figure 4 Effects of retention rate for various mass fractions of retention aids (D-PEO^a-0, D-PEO^a-1 and PAM).

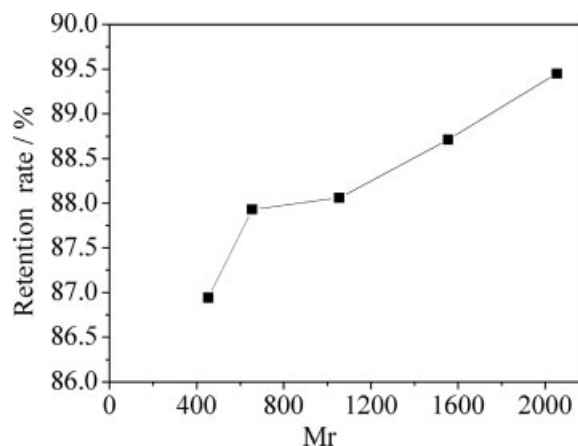


Figure 5 Effect of the PEO-A Mr value on the retention rate (monomer molar feed ratio G6.0 PAMAM : DAC : PEO-A = 1 : 128 : 128, mass fraction of retention aid = 0.2%).

and static electric sorption, in which fines or fillers could be captured and then agglomerated by fibers. The flocculation efficiency of D-PEO^a-1 was superior to that of D-PEO^a-0 and PAM. The effect of the PEO-A M_r value on the pulp retention rate is shown in Figure 5. The dendrimer retention rate increased with an increasing PEO-A M_r value. According to the basic principle of PEO flocculation, the flocculability of PEO-A improved with an increasing PEO chain length, so the PEO-A M_r value was higher and the retention of pulp fines was better.

CONCLUSIONS

PEO-grafted cationic dendrimers were synthesized on the basis of a G5.0 PAMAM dendrimer, with the PEO macromonomer and DAC groups on the surface of the dendrimers via a Michael addition reaction. FTIR, ¹H-NMR, ¹³C-NMR, and elemental analysis were used to characterize the new dendrimers. These results demonstrated that the prepared dendrimers were composed of chain units of G5.0 PAMAM, DAC, and PEO. The experiments with the dendrimers as retention aids for pulp fibers exhibited excellent retention efficiency. They may have potential as new paper retention aids in papermaking.

References

1. Hecht, S. J. *Polym Sci Part A: Polym Chem* 2003, 41, 1047.
2. Tomalia, D. A. *Prog Polym Sci* 2005, 30, 294.
3. Vögtle, F.; Gestermann, S.; Hesse, R.; Schwierz, H.; Windisch, B. *Prog Polym Sci* 2000, 25, 987.
4. Shin, J. H.; Han, S. H.; Sohn, C. *Tappi J* 1997, 80, 179.
5. Allen, L.; Polverari, M. *Nordic Pulp Pap Res J* 2000, 15, 407.
6. Koper, G. J. M. *J Pulp Pap Sci* 1999, 25, 81.
7. Zhou, G.-Z.; Tan, H.-M.; Luo, Y.-J. *Environ Sci Technol* 2003, 26, 1.
8. Peng, X.-C.; Peng, X.-H.; Zhao, J.-Q.; Lin, Y.-W. *Petrochem Technol* 2005, 34, 986.

9. Peng, X.-C.; Peng, X.-H.; Zhao, J.-Q. *Nanoscience* 2005, 1, 146.
10. Al-jamal, K. T.; Sakthivel, T.; Florence, A. T. *J Pharm Sci* 2005, 94, 102.
11. Sarbolouki, M. N.; Sadeghizadeh, M.; Yaghoobi, M. M.; Karami, A.; Lohrasbi, T. *J Chem Technol Biotechnol* 2000, 75, 919.
12. Engel, G. D.; Gade, L. H. *Chem Eur J* 2002, 8, 4319.
13. Wang, S.; Gaylord, B. S.; Bazan, G. C. *Adv Mater* 2004, 16, 2127.
14. Kojima, C.; Kono, K.; Maruyama, K.; Takagishi, T. *Bioconjugate Chem* 2000, 11, 910.
15. Jang, W. D.; Nishiyama, N.; Zhang, G. D.; Harada, A.; Jiang, D. L.; Kawauchi, S.; Morimoto, Y.; Kikuchi, M.; Koyama, H.; Aida, T.; Kataoka, K. *Angew Chem Int Ed* 2005, 44, 419.
16. Unal, S.; Lin, Q.; Mourey, T. H.; Long, T. E. *Macromolecules* 2005, 38, 3246.
17. Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polymer* 1985, 17, 117.
18. Peng, X.-H.; Shen, J.-R.; Xiao, H.-N. *J Appl Polym Sci* 2006, 101, 359.